

**Reduced-Temperature, Electrode-Supported, Planar (RTESP) Solid Oxide Fuel Cells
(SOFC)**

by

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ABSTRACT

Research effort at the University of Utah and Materials and Systems Research, Inc. (MSRI) is on anode-supported, planar solid oxide fuel cells (SOFC). The overall objective of the current effort is to demonstrate SOFC stacks of up to 2 kW capacity operating at a temperature below 800°C. This manuscript describes some of the results on single cells as well as on small stacks. Single cells used for studying the role of electrode microstructure are typically 2 to 3 cm in diameter with an active area of 2 cm². Cells used for stack testing are square-shaped with an active area of about 25 cm². The interconnect used is configured using a 5 mil metallic foil. Early work on stacks was on externally manifolded cells. This has led to six-cell stacks with power as high as 60 W at 800°C with hydrogen as the fuel and air as the oxidant. Recently, however, the effort has been shifted to internally manifolded cells and preliminary work has been very encouraging. Specifically, four-cell stacks with power of ~22 W have been tested. This translates into performance as high as 1.14 liters/kW (~0.88 kW/liter as the stack power density on a volumetric basis). These are preliminary results. Based on prior stack tests using external manifolding, significant further improvements are anticipated. The most important findings are: (1) The cells can be assembled into stacks without a glass seal, and can be readily disassembled after the test. (2) The cells can be heated and cooled without failure. Preliminary experiments have been done on small single cells as a function of the water content of the fuel. The objective was to investigate cell performance in depleted fuels. Single cell tests were also done as a function of anode thickness which was varied between ~1 and ~4 mm.

I. INTRODUCTION

The typical materials used in the state-of-the-art fuel cells are as follows: (1) Cathode – Sr-doped LaMnO₃ (LSM), (2) Electrolyte – Y₂O₃-doped ZrO₂ (YSZ), and (3) Anode – Ni + YSZ. In many cases, YSZ is added to LSM to enhance the electrocatalytic activity. Current efforts in solid oxide fuel cells can be categorized on the basis of the supporting component of the three component (cathode/electrolyte/anode) structure; electrode-supported or electrolyte-supported [1]. The electrolyte-supported cells use YSZ membranes of > 150 μm thickness. The ohmic contribution of the electrolyte at 800°C alone is in excess of 0.75 Ωcm². As such, electrolyte-supported fuel cell systems with YSZ electrolyte are unsuitable for operation at temperatures typically below 900°C with reasonable performance. This also necessitates the use of ceramic interconnects, or expensive, high chromium metallic interconnects. In electrode-supported fuel cells, the supporting component can be either the cathode or the anode. In these designs, the electrolyte thickness is typically between 5 and 30 μm, while the electrode thickness can be between ~250 μm and ~2 mm. In the cathode-supported design, the YSZ electrolyte and the cathode thermal expansion coefficients are well-matched which places no restriction on the electrolyte thickness. In the anode-supported cells, the thermal expansion coefficient of the anode is greater than that of the YSZ electrolyte. This places an upper limit on the electrolyte thickness, which is typically about 30 μm. The anode-supported cell design offers the following advantages over the cathode-supported design. (1) The concentration polarization is lower since the effective binary diffusivity of the anode gas is typically 3 to 4 times greater than that of air [2]. Thus, it is preferable to make the anode thicker. (2) The presence of metallic nickel in the anode leads

to a better thermal shock resistance due to its higher thermal conductivity and plasticity. (3) Since the requisite porosity is readily created by reducing NiO to Ni, the desired electrode microstructure can be readily developed in anode-supported cells. For these reasons, the effort at MSRI and the University of Utah has been on anode-supported cells. In laboratory-sized cells, maximum power densities as high as 1.9 W/cm^2 at 800°C with hydrogen as the fuel and air as the oxidant have been demonstrated in our work. In what follows, some aspects of the current work at MSRI and the University of Utah is described.

III. EXPERIMENTAL PROCEDURE

Cell Fabrication: The typical cell fabrication procedure consists of the following steps. (1) Green-forming of the anode-support using a powder mixture of NiO and YSZ. This is done using die-pressing for small laboratory-sized cells, or by tape-casting for square-shaped cells of 5 cm x 5 cm (active area) dimensions. The cell thickness is typically between 0.5 and 2 mm. (2) Deposition of the YSZ electrolyte layer by painting, dip-coating or spray-coating using a suitable liquid medium. (3) Sintering of the electrolyte/anode assembly at a temperature between 1400 and 1450°C . (4) The application of cathode and firing at a temperature between 1000 and 1200°C . This completes the cell fabrication procedure. Reduction of NiO to Ni is accomplished during cell testing.

A selected number of samples of anode materials were fabricated by die-pressing followed by sintering using different amounts of NiO and YSZ. Also, a few samples were made with tetragonal zirconia containing 3 mol.% Y_2O_3 (TZP). These samples were made to investigate mechanical properties of the anode as a function of nickel content, and the role of yttria content in zirconia.

Measurement of Strength of Anodes: Separate anodes made with varying amounts of nickel content, and containing two different types of zirconia (8 YSZ and 3 TZP) were fractured in flexure to determine their strength.

Cell and Stack Testing: The set-up and the procedure used for testing single cells was described in [3]. The set-up consists of two alumina tubes with inconel bushings in between which a cell is secured. Electrical contacts are made using noble metal wires and meshes. The fuel used is humidified hydrogen and the oxidant is air. Typical cell tests are conducted over a range of temperatures between 650 and 800°C . A few tests were conducted using fuel containing various amounts of water. This was achieved by varying the bubbler temperature. The objective of these experiments was to simulate the expected behavior of cells under varying degrees of fuel utilization. A few experiments were conducted where the anode thickness was varied over a wide range (between about 1 mm and 4 mm). The objective of these experiments was to assess the possible role of concentration polarization and determine how thick a cell can be without significantly degrading performance. Clearly, the thickness of the anode in these cells was considerably greater than contemplated from a practical standpoint.

Stack Testing: Prior work on stack testing in our laboratory has been on externally manifolded cells. While excellent performance was demonstrated (0.5 W/cm^2 at 800°C in

stacks), sealing between the stack and the manifolds was often problematic (although sealing between cells was good). Recently, as mentioned earlier, our effort has been redirected towards the demonstration of internally manifolded stacks. Preliminary stack testing has been initiated.

Microstructural Characterization: Scanning electron microscopy (SEM) was used to examine the typical microstructures of the cells.

III. RESULTS AND DISCUSSION

Mechanical Properties: (a) Flexural Strength of Ni + YSZ Anodes: Figure 1 shows the flexural strength of Ni + YSZ anodes tested in three point bending. It is observed that Ni + YTZP anodes are consistently stronger than Ni + YSZ. This is consistent with expectations since YTZP is known to be considerably stronger than YSZ and is a well known structural ceramic. Interestingly, however, it is observed that with increasing nickel content, the strength of Ni + YTZP decreases while that of Ni + YSZ increases. While the strength of two-phase materials can not be described in terms of rules of mixture, it would appear that the strength of Ni is intermediate to that of (porous) YSZ and YTZP. The strongest Ni + YTZP had a strength in excess of 300 MPa, and the weakest Ni + YSZ had a strength in excess of 100 MPa. Despite the higher strength of Ni + YTZP, no further work was done since it is known that YTZP undergoes phase destabilization and strength degradation if exposed to moisture in the temperature range from 100 to 300°C. Since fuel cell stacks will almost certainly have to be thermally cycled through this range, its use in an anode may pose potential problems. For this reason, all of the work in the current project is done with Ni + YSZ anodes.

(b) Issues Concerning the Potential for Delamination: The thermal expansion coefficient of YSZ is smaller than that of a mixture of NiO and YSZ, or of Ni and YSZ. Thus, a thin film of YSZ electrolyte deposited on the anode is in a state of biaxial compression at a temperature below the sintering temperature. Since the cells are cooled to room temperature after sintering, the maximum level of stress is expected at room temperature. The existence of a biaxial compression ensures that the YSZ film will not crack. However, it is possible that the film will delaminate if its thickness is too large.

Figure 2 shows a schematic of a YSZ film of thickness h on an anode of thickness d . The Young's modulus of YSZ is E_1 , the Poisson's ratio is ν_1 , and the coefficient of thermal expansion is α_1 . The Young's modulus of the anode is E_2 , the Poisson's ratio is ν_2 , and the coefficient of thermal expansion is α_2 . The calculations given here are for $d \gg h$. It can be shown that the delamination will occur provided [4]

$$(\alpha_2 - \alpha_1)(T_2 - T_1) = |\Delta\alpha\Delta T| \geq \sqrt{\frac{2\gamma_{fm}(1-\nu_1^2)}{hE_1}} \quad (1)$$

or if

$$h \geq \frac{2\gamma_{fm}(1-\nu_1^2)}{E_1(\Delta\alpha\Delta T)^2} \quad (2)$$

where γ_{fm} is the interfacial fracture surface energy for delamination. The above criterion can be readily written in terms of the more conventional elastic energy release rate. For the support thickness much greater than the film thickness, note that the elastic properties of the support are unimportant. For $\alpha_2 = 12 \times 10^{-6} / ^\circ\text{C}$, $\alpha_1 = 10 \times 10^{-6} / ^\circ\text{C}$, $\Delta T = 1300$, $E_1 = 200$ GPa, $\nu_1 = 0.3$, and $\gamma_{fm} = 25 \text{ J/m}^2$, the estimated upper limit of h is $\sim 33 \text{ }\mu\text{m}$. No experimental value for γ_{fm} is available. The assumed value of $\gamma_{fm} = 25 \text{ J/m}^2$ corresponds to a critical fracture toughness is the sliding mode of about $3 \text{ MPa}\sqrt{\text{m}}$ which appears reasonable. The preceding estimate suggests that the YSZ thickness should be typically less than $30 \text{ }\mu\text{m}$. This will of course depend upon the values of the parameters used. Nevertheless, an upper limit of $30 \text{ }\mu\text{m}$ should serve as guide for anode-supported cell design.

Single Cell Testing as a Function of the Bubbler Temperature: Figure 3 shows the voltage vs. current density traces for a single cell tested at 800°C with humidified hydrogen as the fuel and air as the oxidant. The bubbler temperature was varied between 32 and 75°C . The corresponding range for partial pressure of water in the fuel was 0.047 atm to 0.38 atm , and the corresponding partial pressure of hydrogen in the incoming fuel was in the range $\sim 0.95 \text{ atm}$ and $\sim 0.62 \text{ atm}$. The short circuit current density, i_s , is expected to be linearly proportional to the partial pressure of hydrogen. An examination of Figure 3 shows that as the bubbler temperature is increased, the short circuit current density decreases, in accord with the expectation. The ratio of $p\text{H}_2(75^\circ\text{C})/p\text{H}_2(32^\circ\text{C})$ is $\sim 0.62/0.95$ or ~ 0.65 . The corresponding ratio of short circuit current densities, namely, $i_s(75^\circ\text{C})/i_s(32^\circ\text{C})$ is $\sim 3.2/4.6$ or ~ 0.7 , which is in reasonable agreement with expectations. The more important observation from Figure 3 is that the relative difference between the $V-i$ curves at low current densities is much smaller. Since the SOFCs are typically operated at a voltage of 0.7 to 0.75 V , the important parameter is the power density at 0.7 or 0.75 volt . Figure 4 shows the plots of power density vs. fuel utilization at 0.7 V and 0.9 V . The fuel utilization is the projected one for a given water content in the fuel. The figure shows that at 0.7 V , the decrease in power density between $\sim 5\%$ and $\sim 38\%$ (local) fuel utilization is modest. At 0.9 V , there appears to be slight increase in the power density with increased local fuel utilization (depleted fuel) followed by the expected decrease. It is believed that this slight increase may be related to a decrease in polarization losses.

The Effect of Anode Thickness on Cell Performance: These experiments were conducted to determine the role of anode thickness, which is the supporting component of the cell. Although in practice, the anode thickness is not expected to be greater than 2 mm (and may be considerably smaller), in the present work cells with anode thickness approaching 4 mm were made to investigate the effects of concentration polarization at the anode. Details of this work are published elsewhere [5]. Cells were tested at 800°C with humidified hydrogen as the fuel and air as the oxidant. Figure 5 shows a plot of the measured power density vs. anode thickness. It is seen that maximum power density exceeding 1 W/cm^2 was achieved with anode thickness approaching 4 mm . This shows that high power densities can be realized even with relatively thick anodes. At the same time, for a cell with an anode thickness of about 1 mm , the maximum power density was about 1.9 W/cm^2 . This suggests that the effects of anodic concentration polarization can be significant at large anode thicknesses.

Evaluation of Cells in Internally Manifolded Stacks: Our earlier work was on stack testing using cells made by die-pressing followed by sintering. Also, the earlier work was on externally manifolded cells. The data on these stacks was reported previously. As mentioned earlier, the effort recently has been redirected towards the development of cells by tape-casting followed by sintering, a process readily amenable to mass production. Also, the cells of the new design are internally manifolded. Figure 6 shows the results of a four cell stack test. The procedure for stack assembly consists of stacking the cells with a metallic interconnect separator without rigid cells. The cells thus are fully free to expand and contract, and thus can be thermally cycled with no degradation. In fact, the cells used in this stack test had been used three times with different interconnect and assembly procedures. A significant point to note is that the attainment of theoretical OCV, which indicates good sealing. The maximum power of about 22 W was achieved in an active volume of about 25 cm³; that is about ~1.14 liter/kW. Based on prior experience, substantial improvements are expected beyond this once extraneous sources of voltage losses are minimized. The principal losses in this stack were attributed to contacts between various parts. Strategies for lowering the losses are being implemented.

IV. SUMMARY

Anode-supported cells for operation below 800°C were fabricated by two approaches: (1) Die-pressing of anode precursor powder, dip-coating (slurry-coating or spray-coating) a YSZ layer, followed by sintering. (2) Tape-casting of anode precursor, spray-coating the surface with a YSZ layer, followed by sintering. The performance of single cells was evaluated as a function of water content of the incoming fuel, which was varied over ~4% to ~38%. The objective was to investigate the performance characteristics as a function fuel depletion. This effectively provides a measure of cell performance at various levels of fuel utilization. It was demonstrated that in single cells, power densities exceeding 0.8 W/cm² at 0.7 V could be realized at 800°C for fuel containing ~38% water. Single cell performance was also examined as a function of anode thickness which was varied between ~1 and ~4 mm. The objective was to determine the upper limit of the anode thickness without seriously compromising performance. Maximum power density at 800°C at an anode thickness of 1 mm was measured to be as high as 1.9 W/cm², and at an anode thickness of ~4 mm, as high as 1.1 W/cm² was measured. Preliminary four cell stack tests are promising. These stacks were internally manifolded. The cells could be thermally cycled without degradation and the sealing is flexible without any glass. Thus, the same cells could be tested repeatedly by reassembling them with different interconnects or other modifications. The OCV was near theoretical indicating good sealing. The stack maximum power was about 22 W. Further significant improvements are expected once losses associated with contacts are minimized. However, even at this preliminary stage, the measured power translates into a power density (active volume) of ~0.88 kW/liter (~1.14 liter/kW) on a volumetric basis.

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References:

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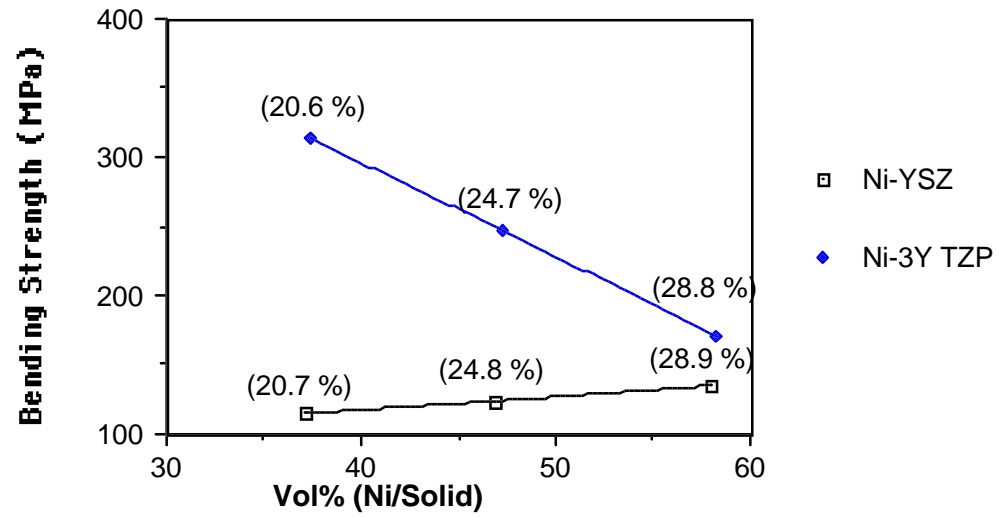


Figure 1: Bending strength of Ni + YSZ and Ni + 3Y TZP anodes as a function of vol.% Ni. The numbers in parentheses indicate the estimated porosities.

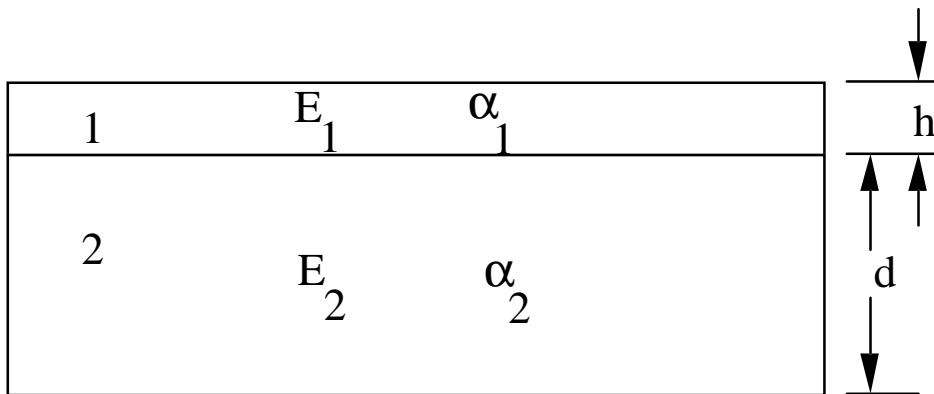


Figure 2: A schematic showing a film of YSZ (Young's modulus E_1 , and coefficient of thermal expansion α_1) of thickness h , deposited on an anode (Young's modulus E_2 , and coefficient of thermal expansion α_2) of thickness d . The calculations given are for $d \gg h$.

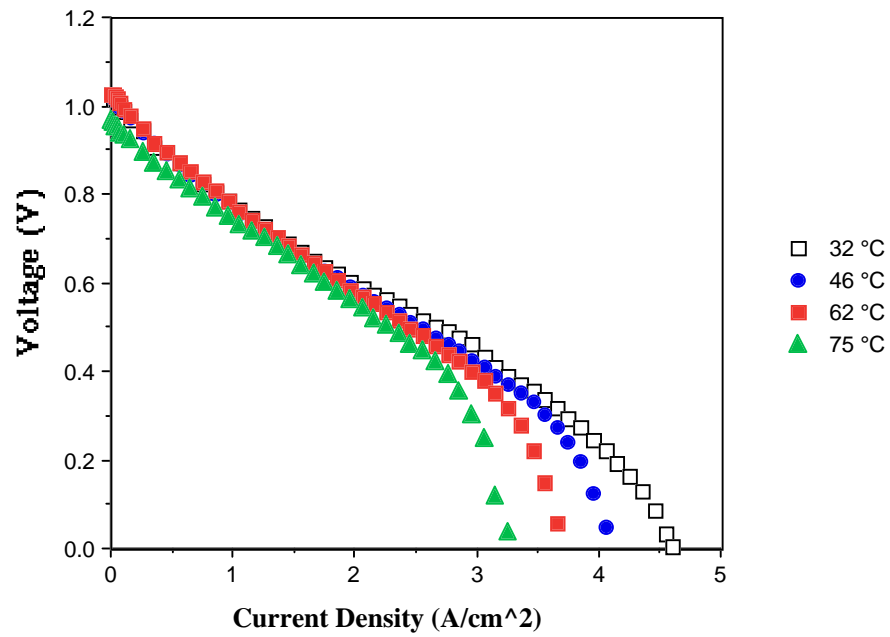


Figure 3: Voltage vs. current density traces for a single cell tested at 800°C with humidified hydrogen as the fuel and air as the oxidant. The bubbler temperature was varied between 32 and 75°C.

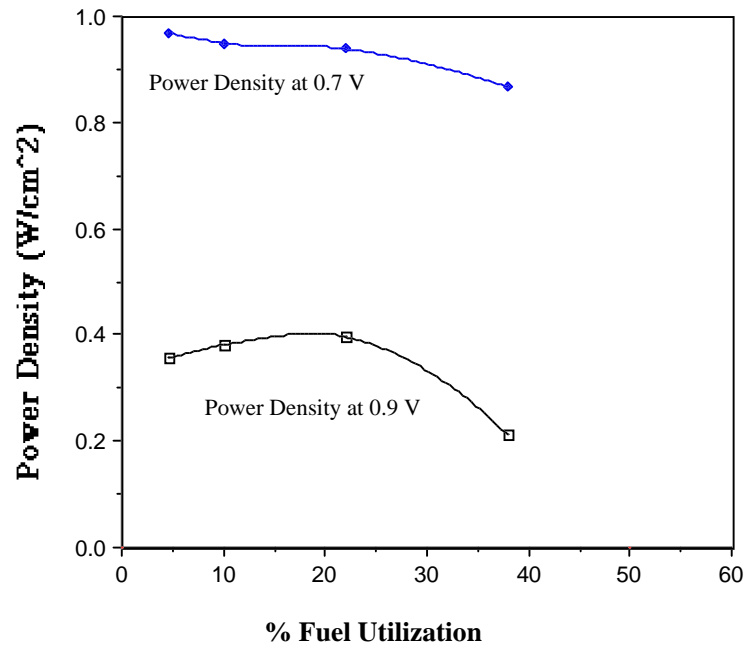


Figure 4: Power density as a function of % fuel utilization, as estimated from the water content of the fuel at two values of voltage; 0.7 volt and 0.9 volt.

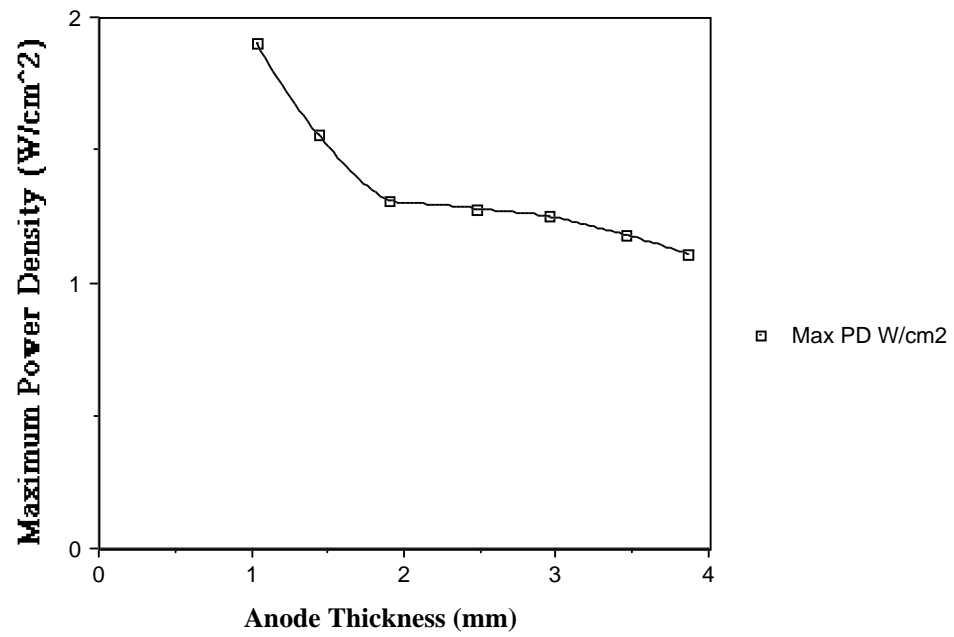


Figure 5: Maximum power density as a function of anode thickness for cells tested at 800°C.

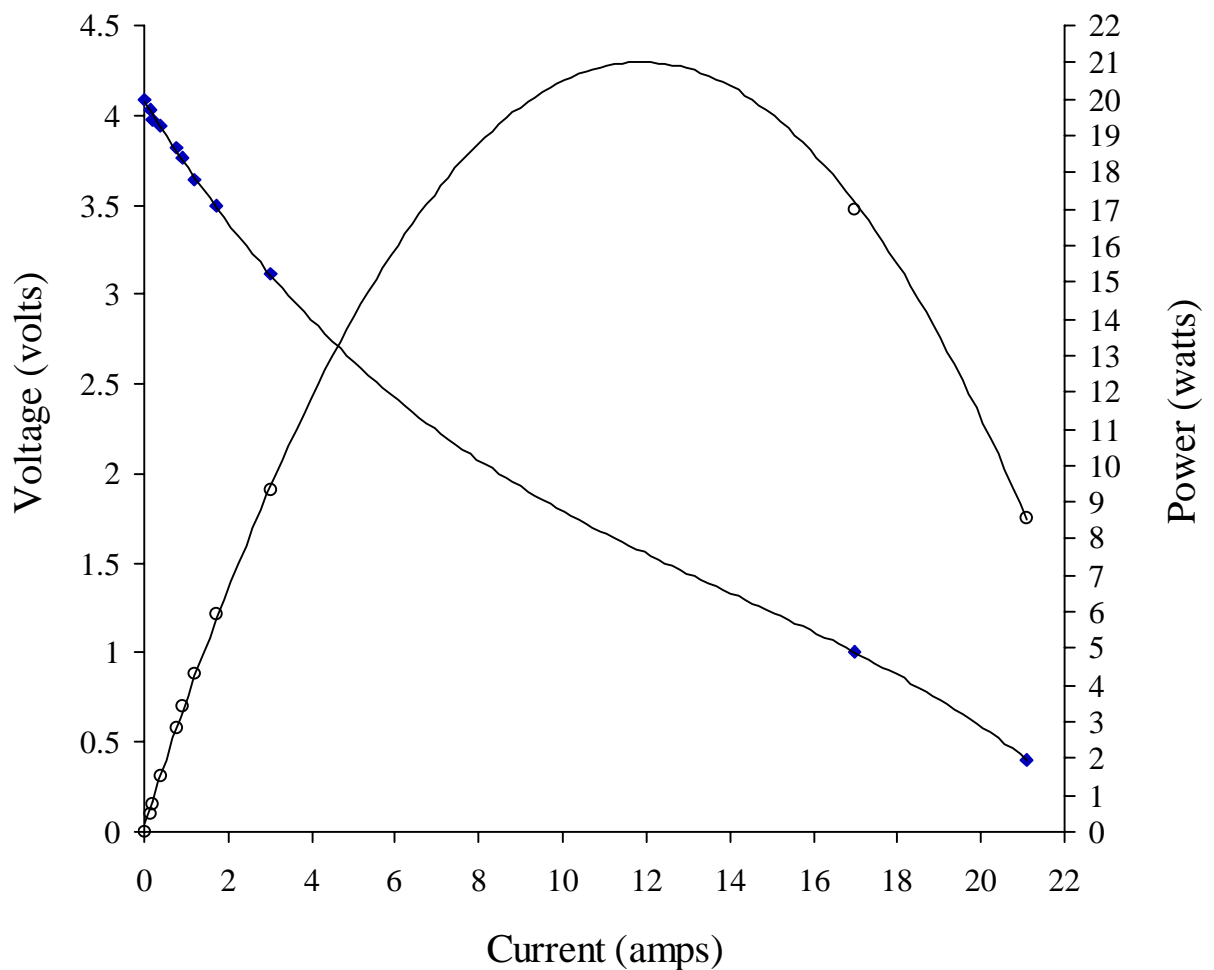


Figure 6: Voltage and power density vs. current density for a four cell, internally manifolded stack with metallic interconnect tested at 800°C. The cells are fully free to expand and contract, and there is no rigid seal. These cells have been tested in stacks three times with different variations of the interconnect and other assembly and testing procedures. Stack was tested for 180 hours with stable performance after which the test was voluntarily terminated. Several new alterations are currently being implemented.